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# FP-33 Final Analysis Report

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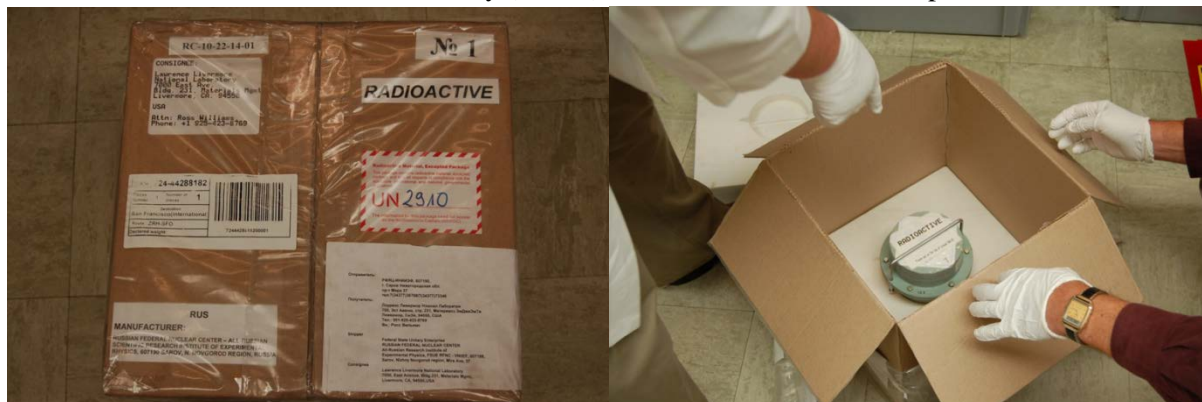
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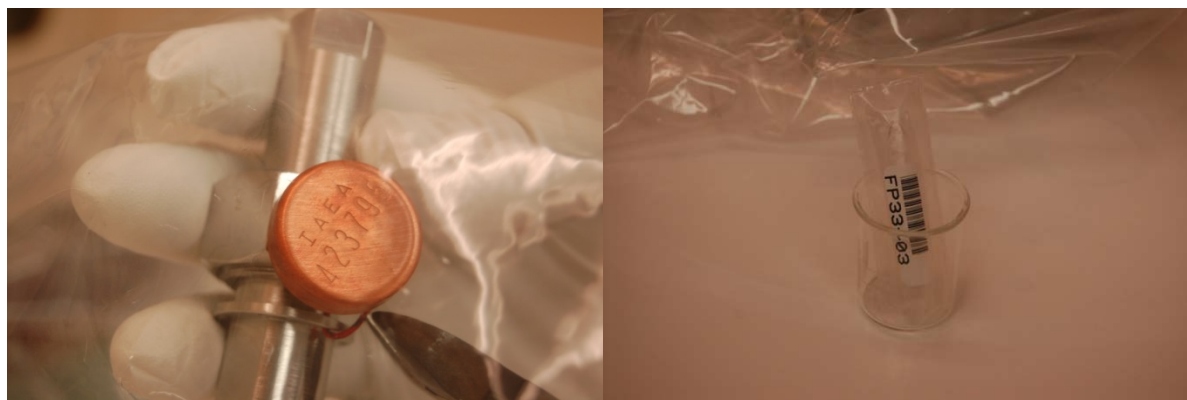
## FP-33 Final Analysis Report

### 1. Sample Receipt and Unpacking

The test samples of the final product of the mass separated  $^{244}\text{Pu}$  from VNIIEF (FP-33) were received at Lawrence Livermore National Laboratory (LLNL) on 5-Jan-2015 and were unpacked on 6-Jan-2015.



The seal (IAEA 369807) on the TUK-35 container was intact. One sample was removed on 6-Jan-2015 and the seal (IAEA 423795) on this sample was intact.



The sample inside this container was FP33-03. The plastic bags were removed, and the ampoule (marked with a 3) was weighed on 7-January-2015. The weight was 3.1030 grams. On 10-Jan-2015, glass ampoule FP33-03 was weighed again and found to be the same: 3.1030 grams. It is stored for later use as may be necessary.

The other two ampoules in the TUK-35 container were removed on 9-Jan-2015.



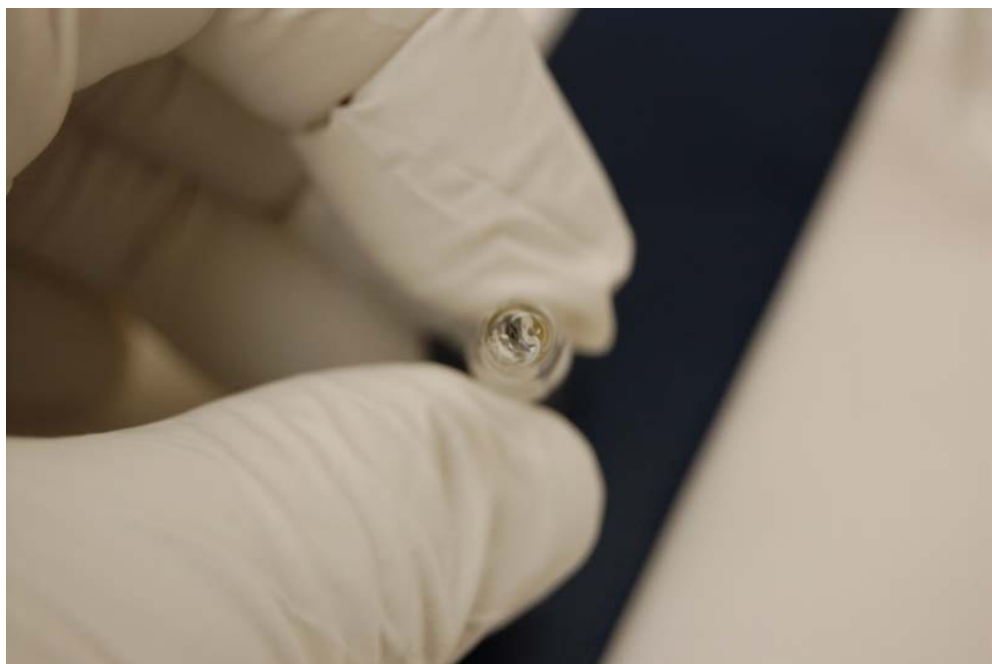
Sample FP33-01 was contained within the steel sleeve with IAEA seal 423794. This seal was intact. The glass ampoule was removed from the steel sleeve and the plastic sleeves, and was in good condition. The ampoule was marked with the number 1. The weight of this ampoule was 2.9049 grams.



Sample FP33-02 was contained within the steel sleeve with IAEA seal 423793. The seal was intact. Inspection revealed that this vial had leaked. The written mark on the glass ampoule (the number 2) was legible, but it had faded in color (not dark black) due to exposure to acid fumes inside the plastic sleeve. The ampoule was defective, and a significant amount of liquid had been lost, and so an accurate Pu content measurement of this vial would not be possible. However, the contents remaining in the ampoule should be suitable for isotopic composition measurements.



Sample FP33-02 with sharpie mark removed. The ampoule was wiped clean and dried before weighing. The weight of the ampoule was 2.6208 grams.



The top of vial FP33-02. The photograph seems to reveal the cause of the leakage: an orifice in the heat sealed end. That is, the vial was not sealed at origin. It was opened and diluted for measurements of the isotopic composition. Despite filing a good score line, the vial shattered in many pieces on opening. The liquid was policed into a teflon vial with rinses of 4 M  $\text{HNO}_3$ .

## 2. Pu concentration measurements

The Pu content of glass ampoule FP33-01 was measured by isotope dilution mass spectrometry. Two independent measurements were made, one using a  $^{239}\text{Pu}$  spike and the other using a  $^{242}\text{Pu}$  spike. Past experience had shown that opening and quantitatively removing solutions from within these glass ampoules was problematic. The ampoules do not have a drawn end with a defined “snap-point”. Instead, a score line must be filed. Even if a score line is filed completely around the ampoule, it may break and shatter irregularly when snapped. In order to quantitatively recover the solution from within, the following method was used. First, the weight of the vial with a filed score line was determined by weighing within an empty dry 30 mL Teflon PFA vial. Static eliminating devices were used for all weighing, and the balance readings were reproducible. The vial was snapped open over a clean plastic tray and then placed back inside the Teflon vial with all of the glass shards that could be recovered, and reweighed. A 4 M  $\text{HNO}_3$  solution was added to the Teflon vial to completely submerge the opened glass vial, and the Teflon vial was weighed again to determine the weight of solution added. The weights are given in the following table. This work was done on 10-Jan-2015.

<b>SAMPLE FP33-01</b>	(g)	Std. Uncert.
Wt. of glass ampoule (as received):	2.9049	0.00007
MT, Labeled 30 mL Savillex vial:	46.2738	0.00007
Plus glass ampoule with filed score inside:	49.1677	0.00007
Weight of glass ampoule with filed score:	2.8939	0.0001
With opened vial and glass shards:	49.1630	0.00007
Wt. of sample lost:	0.0047	0.0001
Wt. % of sample lost:	0.162	
Wt. with added 4 M $\text{HNO}_3$ :	73.4596	0.0001
Wt. of 4 M $\text{HNO}_3$ added:	24.2966	0.00012

Additional uncertainties are introduced by this method because 1) the recovery of the sample is not complete, 2) there is liquid inside the ampoule and that unknown mass must be added to the weight of the 4 M  $\text{HNO}_3$  that is added, and 3) no buoyancy corrections were made for the mass of the glass was weighed in acid solution, rather than in air. The weight of acid contained within the ampoule was estimated to be  $0.1 \pm 0.05$  grams (a 50% standard uncertainty). This weight was added to the weight of the dilution solution to obtain the total weight of FP33-01 Dilution ( $24.3966 \pm 0.05$  grams). The sample in the Teflon vial was shaken periodically and sonicated to homogenize it. Samples of this solution were aliquoted on 24-Jan-2015 for the concentration measurements by isotope dilution.

The data for the two spikes used for isotope dilution mass spectrometry (IDMS) and the weights of the sample aliquots are given in the following tables.

FP33-01 x $^{239}\text{Pu}$			FP33-01 x $^{242}\text{Pu}$		
Spike: LLNL RAT_STD		Std. Uncert.	Spike: NIST SRM 4334H		Std. Uncert.
$^{239}\text{Pu}$ atoms/g-spike	4.6808E+12	1.53E+10	$^{242}\text{Pu}$ atoms/g-spike	4.8874E+12	1.76E+10
g-spike	0.5138	0.00007	g-spike	0.5336	0.00007
g-FP33-01 Dilution	0.5660	0.00006	g-FP33-01 Dilution	0.5678	0.00007
g-Dilution / ampoule	24.3966	0.05	g-Dilution / ampoule	24.3966	0.05

All analyses were made with the LLNL NuPlasma-HR Multi-Collector ICPMS (MC-ICPMS). The collector configuration used for the IDMS measurements is given in the following table.

	NuPlasma MC-ICPMS collector configuration and instrumental methods used for IDMS measurements					
	H3 Faraday	not active	H1 Faraday	not active	L1 Faraday	L2 Faraday
Sample Analyses	244Pu	not active	242Pu	not active	not active	239Pu
Standard Analyses	not active	not active	242Pu	241Pu	240Pu	239Pu

NBL CRM 137 Pu was measured before and after the sample analyses to determine the instrumental mass bias correction factor, and all atom ratio results were corrected using the exponential mass bias correction formula. (See for example, *Uncertainty in Measurement of Isotope Ratios by Multi-Collector Mass Spectrometry*, LLNL-CONF-455394 ). The IDMS analyses were made on 5-Feb-2015, and the results are given in the following table.

		Atomic ratios corrected for instrumental mass bias determined from bracketing analyses of CRM 137					
		Pu 239/242		Pu 244/239		Pu 244/242	
Sample ID	Measurement	Result	Uncert. (k=1)	Result	Uncert. (k=1)	Result	Uncert. (k=1)
FP33-01 x 239Pu	assay calibration	2360	560	1.4592	0.0044	3445	817
FP33-01 x 242Pu	assay calibration	0.000036	0.000242	-2800	14300	1.3461	0.0016

The <sup>244</sup>Pu content of FP33-01 in microgram/ampoule and the uncertainty budgets for these analyses are given in the following tables.

	244Pu conc. µg/ampoule	
Sample ID	Result	Uncert. (k=2)
FP33-01 x 239Pu	0.06130	0.00060
FP33-01 x 242Pu	0.06113	0.00053

244Pu conc. µg/ampoule	Uncert. (k=2)		244Pu conc. µg/ampoule	Uncert. (k=2)
0.06130	0.00060		0.06113	0.00053
Uncertainty Budget	%		Uncertainty Budget	%
Pu 244/239 Measurement	37.974		Pu 244/242 Measurement	7.593
Spike concentration	44.361		Spike concentration	69.657
Spike weighing	0.079		Spike weighing	0.094
Sample weighing	0.043		Sample weighing	0.083
Dilution preparation	17.543		Dilution preparation	22.573
	100.000			100.000

An independent quality control analysis of CRM 137 was made during this analytical session and the results are given below with the certified value for this reference material.

Date	Sample ID	240Pu/239Pu	2-s	241Pu/239Pu	2-s	242Pu/239Pu	2-s
2/1/2015	CRM 137 Certified	0.24080	0.00029	0.007390	0.000021	0.015610	0.000052
2/5/2015	CRM 137 QC	0.24082	0.00029	0.007403	0.000018	0.015574	0.000056

### 3. Pu isotopic composition measurements

Four analyses of the isotopic composition were made: two analyses of material from FP33-01 and two analyses of material from FP33-02. While there is some indication that the  $^{239}\text{Pu}/^{244}\text{Pu}$  ratio and the  $^{240}\text{Pu}/^{244}\text{Pu}$  ratio in FP33-02 is slightly higher than FP33-01, the results overlap at the 95% confidence level. The individual results and the mean of all four analyses are given in the following tables.

Ampoule number:		FP33-01		Ampoule gross weight:		2.9049 grams		Measurement date:		12-Jan-15	
		Pu 239/244		Pu 240/244		Pu 241/244		Pu 242/244			
Date/Time	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	
1/12/15 13:38	0.00001148	0.00000018	0.00003975	0.00000049	0.000000924	0.000000026	0.00010189	0.00000072			
1/12/15 15:50	0.00001152	0.00000019	0.00003966	0.00000048	0.000000918	0.000000029	0.00010093	0.00000070			

Ampoule number:		FP33-02		Ampoule gross weight:		2.6208 grams		Measurement date:		13-Jan-15	
		Pu 239/244		Pu 240/244		Pu 241/244		Pu 242/244			
Date/Time	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	Result	U (k=2)	
1/13/15 13:53	0.00001180	0.00000018	0.00004022	0.00000051	0.000000958	0.000000028	0.00010293	0.00000110			
1/13/15 15:36	0.00001179	0.00000018	0.00004021	0.00000050	0.000000897	0.000000029	0.00010144	0.00000108			

FP33 Average (n=4)							
239Pu/244Pu	U (k=2)	240Pu/244Pu	U (k=2)	241Pu/244Pu	U (k=2)	242Pu/244Pu	U (k=2)
0.000011647	0.000000184	0.000039962	0.000000496	0.000000924	0.000000028	0.000101799	0.000000898

atomic percent									
239Pu	U (k=2)	240Pu	U (k=2)	241Pu	U (k=2)	242Pu	U (k=2)	244Pu	U (k=2)
0.001165	0.000018	0.003996	0.000050	0.0000924	0.0000028	0.010178	0.000090	99.98457	0.00014

The collector configuration used for the isotopic composition measurements is shown in the following table. All of the samples, including the analysis of standards for the instrumental mass bias correction and the quality control standards, were analyzed using this two cycle peak-hopping method.

NuPlasma MC-ICPMS collector configuration and instrumental method used for IC measurements							
	Ax Faraday	L1 Faraday	L2 Faraday	IC0	L3 Faraday	IC1	IC2
Cycle 1	not used	244Pu	not used	242Pu	241Pu	240Pu	239Pu
Cycle 2	244Pu	not used	242Pu	241Pu	240Pu	239Pu	not used

The gray shading indicates that the data collected on a given detector for that cycle was not used in any of the calculations. The two cycle routine is required so that all of the minor isotopes in the  $^{244}\text{Pu}$  sample can be analyzed using a SEM pulse-counting detector. These are designated IC0 for ion counter number zero, etc. The ion counter efficiencies relative to the Faraday array are determined from measurements of NBL U010 that are made during the analytical session. NBS SRM 948, which is the same as NBL CRM 138 Pu standard was analyzed at the beginning and end of each session to correct for instrumental mass bias. The biased results for these analyses are given in the following tables.

Date/Time	Sample ID	Measurement	Plutonium isotope ratios	
			Pu 240/239	
			Result	U (k=2)
1/12/15 14:07	NBS SRM 948	determination of mass discrimination	0.08673	0.00051
1/12/15 16:19	NBL CRM 138		0.08696	0.00051

Date/Time	Sample ID	Measurement	Plutonium isotope ratios	
			Pu 240/239	
			Result	U (k=2)
1/13/15 12:58	NBS SRM 948 NBL CRM 138	determination of mass discrimination	0.08717	0.00060
1/13/15 16:05	NBS SRM 948 NBL CRM 138		0.08739	0.00060

The certified value for  $^{240}\text{Pu}/^{239}\text{Pu}$ , corrected to the date of analysis is:

Standard Reference Values			
Date	Sample ID	240Pu/239Pu	2-s
1/12/2015	NBS 948 = CRM 138	0.08614	0.00011

The results for the quality control standards analyzed during these analytical sessions are given in the following tables.

Date/Time	Sample ID	Measurement	Plutonium isotope ratios					
			Pu 240/239		Pu 241/239		Pu 242/239	
			Result	U (k=2)	Result	U (k=2)	Result	U (k=2)
1/12/15 15:04	CRM 137	calibration check	0.2415	0.0016	0.06314	0.00051	0.01543	0.00019
1/12/15 16:47	CRM 137		0.2418	0.0016	0.06367	0.00050	0.01560	0.00019

Date/Time	Sample ID	Measurement	Plutonium isotope ratios					
			Pu 240/239		Pu 241/239		Pu 242/239	
			Result	U (k=2)	Result	U (k=2)	Result	U (k=2)
1/13/15 14:50	CRM 137	calibration check	0.2398	0.0018	0.00731	0.00011	0.01539	0.00022
1/13/15 16:51	CRM 137		0.2397	0.0018	0.00742	0.00010	0.01541	0.00022
1/13/15 16:28	CRM 122		0.1316	0.0010	0.002471	0.000049	0.002078	0.000049

The certified values for these standards are:

Date	Sample ID	240Pu/239Pu	2-s	241Pu/239Pu	2-s	242Pu/239Pu	2-s
1/12/2015	CRM 137	0.24080	0.00013	0.0074265	0.0000036	0.0156101	0.0000044
1/12/2015	CRM 122	0.131892	0.000046	0.0028380	0.0000034	0.002052	0.000015

All of the quality control analyses are in agreement with the certified values with the exception of the  $^{241}\text{Pu}/^{239}\text{Pu}$  result for CRM 122 measured on 13-Jan-2015. However, this result agrees with many previous measurements of this CRM made at LLNL.

The average uncertainty budget for the isotopic composition measurements is:

FP33 Uncertainty Budgets		% contributions to the combined uncertainty (average of 4 analyses).			
Isotope Ratio		Pu 239/244	Pu 240/244	Pu 241/244	Pu 242/244
Signal Measurement Numerator		7.81	3.24	31.55	3.80
Signal Measurement Denominator		0.00	0.00	0.00	0.00
Blank		1.79	0.06	4.23	0.04
Detector Baseline		0.03	0.00	51.11	0.05
IC Gain Factor		7.20	10.83	4.91	47.43
Mass Bias Standard Measurement		67.26	69.48	6.64	39.50
Mass Bias Standard Certified Value		15.92	16.39	1.57	9.18
		100.00	100.00	100.00	100.00

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